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FIBER-BORNE AND WATER-BORNE CHEMICAL CONTAMINANTS

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PAPER AND PRINTING ENGINEERING COLLEGE

ABSTRACT

The main idea behind this thesis is to work with recycled paper because this is the latest trend due to the environment. Therefore, after checking into an aspect that has little research completed, the idea of the effects of chemical contaminants on sizing of paper, AKD in particular, was developed. To allow for expansion on this thesis topic, another student will be looking at the effect of chemical contaminants on sizing of the recycled paper.

The experiment contained water-borne chemical contaminants and fiber-borne chemical contaminants. Four different chemical contaminants were used including retention aid, defoamer, biocide, and wet strength. The water-borne chemical contaminants were added with the sizing and made into handsheets on the Noble and Wood. The fiber-borne chemical contaminants were added to the pulp, and washed and dried. Then the contaminated pulp was redispersed, sizing agent added and made into handsheets. The tests conducted were Hercules size test and contact angle.

The results for the water-borne chemical contaminants mostly followed the expected results. The retention aid helped the sizing while the defoamer, biocide, and wet strength hindered the sizing. For the fiber-borne chemical contaminants, the retention aid, defoamer, biocide, and wet strength all increased the sizing above the control level. The contact angle determined that small

amounts of AKD give high contact angles, showing full sizing. Plus, the water-borne chemical contaminants had high contact angles for the high HST values, and the fiber-borne chemical contaminants gave high contact angle for the low HST values.

The objective behind this thesis was to determine if the chemical contaminants would adhere to the fiber before the AKD was added, and therefore help or hinder the sizing effect.

INTRODUCTION

The chemical contaminants that enter the papermaking system can effect a number of variables, but this thesis only examined the effect the chemical contaminants have on the sizing of paper. Currently, sizing is a very important aspect in the papermaking industry because the purpose of sizing is to enable paper product to resist penetration by fluids including ink or water. Therefore, there are chemical contaminants that could hinder or help the sizing of the paper. The chemical contaminants that help the sizing of the paper are the contaminants that help retain the sizing element in pulp instead of being washed away with the fines, fillers or white water.

There are two different ways that the chemical contaminants could be introduced into the pulp slurry: water-borne and fiber-borne. The water-borne chemical contaminants are best described as virgin pulp because the contaminants enter the pulp with the water instead of the fiber. The fiber-borne chemical contaminants are best described as recycled paper because the contaminants enter the pulp with the fiber. Recycled pulp is a good example because there are chemical contaminants already adhered to the fiber from the first papermaking process. Therefore, the contaminants enter the process with the fibers.

The reason of the importance in determining the introduction of the chemical contaminants is directly linked to increase use of recycled. If the trend increases to use more and more recycled paper, then the need for cleaner or more chemically free recycled pulp will increase. If chemicals are used in the first pulping process that will enhance the sizing performance when recycled, then that chemical will improve the recyclablility of that fiber.

The experiment contained water-borne chemical contaminants as virgin fiber and fiber-borne chemical contaminants as simulated recycle. Four different chemical contaminants were used including retention aid, defoamer, biocide, and wet strength. The water-borne chemical contaminants were added with the sizing and made into handsheets on the Noble and Wood. The fiber-borne chemical contaminants were added to the pulp, and washed and dried. Then the contaminated pulp was redispersed, sizing agent added and made into handsheets. The test conducted were Hercules size test and contact angle.

GOALS

There were two goals achieved in this thesis experiment. The first was to determine the impact that different levels of chemical contaminants have on the AKD sizing of the sheet. The second was to determine whether there was an impact on the AKD sizing of the sheet by the method that the chemical contaminants were introduced into the pulp.

OBJECTIVE

The contaminants used were retention aid, wet strength additive, defoamer and biocide. Each of these contaminants were injected into the pulp before the drying stage. The idea of this process was to determine if the contaminants stayed attached to the fiber after being washed and dried, and whether their attachment effected sizing. The results did show that the HST values increased when the chemical contaminant attached onto the fiber before the AKD was added.

REASON FOR THIS STUDY

Papermachines today are asked to run faster, recycle more white water, use more secondary fiber and filler, but to perform without breaks, holes and dirt at unprecedented sheet quality requirements. But, there are very few studies that have examined different techniques designed to protect the papermachine from deposits due to contaminants in recycled fibers that cause the breaks, holes, and dirt. Since the literature for recycled fibers is slim, the literature for water-borne and fiber-borne is even less, in fact - none. Therefore, the area of study is undocumented and unresearched and perfect for a topic of a thesis.

BACKGROUND

SIZING AGENT : ALKYL KETENE DIMER

The alkaline sizing of paper presents some significant cost savings to the papermaker. The two most common alkaline sizing agents currently being used are alkenyl succinic anhydrides (ASA) and alkyl ketene dimers (AKD). The generally accepted development of size response is through ester formation with cellulosic hydroxyl groups. Under alkaline conditions through the forward dryers this reaction occurs relatively fast, and on-machine sizing can be obtained from the slower reacting AKD molecule.

AKD is a ketene dimer with two alkyl chains produced from two fatty acid molecules by dimerization of their acid chlorides. As mentioned above, AKD does not hydrolyze as rapidly, and the sizing reaction does not proceed as rapidly as with ASA. Reportedly, newer cationic emulsions have shown increased reactivity with cellulose while not showing increased hydrolysis.

The advantages of alkyl ketene dimers over acid systems include:

- improved sheet strength
- substitution of calcium carbonate for titanium dioxide
- improved paper stability on aging
- reduction in energy consumption
- increased productivity
- reduced corrosion

- increased system closure.

Many of these advantages are interrelated. Optimum conditions should be developed based on each mill or grade and its needs.

The amount of AKD to be added and the furnished used also determine the effectiveness of the sizing agent used. For AKD, adding nominal dosages may not be the most relevant method to measure the amount of AKD present because it is simply the amount of AKD added to the fiber and water slurry. A more appropriate method might be to consider the actual amount of AKD retained or reacted on the fiber. Research demonstrated that both retained and reacted AKD contribute to sizing. Reacted AKD, however, is approximately three times as efficient as retained with unreacted AKD. When it comes to the type of furnish being used, the ratio of three to one becomes closer to one to one. The refined softwood pulp has the highest level for both retained and reacted AKD. This is most likely due to the large increase in fiber surface area that occurs upon refining. The hardwood pulp shows the largest sizing response factor whatever the method of measuring the amount of AKD; therefore, hardwood is the easier furnish to size. Upon research, the nominal dosage of AKD required to achieve a full sizing or a 90 degree contact angle is approximately 0.70 kilograms per metric ton for refined softwood and 0.73 kilograms per metric tone for hardwood. This can be seen on Graph 1, entitled "HST vs. nominal AKD dosage". Up to the value of 0.65, there is no sizing; and after the value of 0.80, there is full sizing with values of at least 2,000 seconds. Therefore, for a refined softwood/hardwood split, a value of 0.70 kilograms per metric ton would be a scientific approximation of full sizing.

Another parameter in determining the resulting penetration behavior of a liquid besides HST, is the contact angle measurement (mentioned above briefly). The contact angle is the angle between the impinging liquid and the sheet surface. It is possible to see the predicted importance of the contact angle on penetration rate by consideration of the Lucas-Washburn theory. This theory states that for situation where the contact angle is greater than 90 degrees, no liquid penetration should occur. But, in truth, for full sizing results, the contact angle is significantly less than 90 degrees. Once again one possible reason for the difference is in the sheet structure between furnishes. Softwood has long and stiff fiber that forms a loose, bulky sheet with large pore radii. Here a contact angle of 90 degrees is necessary to prevent penetration. Both hardwood and refined softwood are much more flexible, however, and form denser sheets with smaller pores. The Lucas-Washburn theory states a drop in penetration rate with decreasing pore size. So, the true measured contact angle for full sizing is 65 - 75 degrees.

To tie the contact angle in with AKD, it is documented that only a relatively small amount of AKD is needed to reach contact angles greater than 90 degrees despite the fiber type. It was stated above that only 0.70 kilograms per metric ton was needed to reach contact angles greater that 90 degrees, which indicate full sizing.

CHEMICAL CONTAMINANTS

Retention Aid

AKD sizes are emulsified with carbonic starches or cationic synthetic polymers which render the size particles cationic. When the size emulsion is added to the paper furnish, it is absorbed quickly and predominately onto the high-surface-area anionic components of the furnish, in particular fines. If effective retention programs for fines are not in place, the high-surface-area fines will not be retained, the potential for size hydrolysis increases, and size efficiency will be reduced.

The literature does describe a number of retention aids that have proven effective in systems containing recycled fibers, including both cationic polymers and nonionic aids such as polyethylene oxide alone or in combination with a phenol formaldehyde resin.

Defoamer and Biocide

Defoamers are used to improve drainage and sheet formation while biocides are used to control slime growth and other microorganisms that occur in the papermaking process. These wet-end additives interfere with sizing response. When using these surface-active agents, it is important to screen them and choose the one that gives minimum resistance.

Wet Strength

Wet strength resins tie fibers and fines together with additional bonds that are not taken apart by water. Wet strength develops during aging. Since wet-strength resins are water-soluble, they must be fixed onto the fibers. Since, wet-strength develops during aging, the best retention on the stock is achieved over a long period of contact.

The direct improvement of web strength is by increasing the relative bonded area, usually by wet-strength additives that are cationic starches, and increasing the fiber-fiber bond by substituting fiber-fiber covalent bonds for the more normal fiber-fiber hydrogen bonds.

The indirect improvement of web strength can occur in two ways. First, wet-strength additives can increase the fines content of the web, which under certain circumstances, can increase the wet densification of the web in the press section of the papermachine. Second, these additives can clean out the fines from the white water of the system, allowing the papermaker to increase the amount of primary refining to which the fibers are subjected.

There is no direct rule that states the extensive use of recycled fibers require the use of large amounts of strength additives to compensate for the loss of strength in repulping. Generally, if normal papermaking parameters prevail, strength additives will behave as they do in conventional papermaking systems.

METHODOLOGY

Two different procedures were taken, one for the water-borne and one for the fiber-borne. But, each procedure used the same level of sizing agent, AKD, which was 0.70 kilograms per metric ton as mentioned in the background. Also, each procedure used the same levels of chemical contaminants. The different between procedures when the sizing agent and chemical contaminant was added to the pulp.

The different levels of chemical contaminant used were based on the levels used in industry. With each chemical contaminant obtained, an estimated amount of that particular concentration used per ton of oven dry fiber was given. This was the low level of contaminant. Then a percentage increase was used to obtain the middle and higher levels of chemical contaminant introduced into the pulp.

The type of furnish used was based on the literature search. The furnish for the ideal retained and reacted AKD results was a combination of refined softwood and hardwood. To follow the industry, a 75/25 softwood/hardwood split was used. The pulp was obtained from the pilot plant as lap pulp.

The methodology for the water-borne chemical contaminants can be seen in Appendix I, Diagram I. A 75/25 softwood/hardwood mix was refined in the Valley Beater in the wet lab until a 450 Canadian Standard Freeness was obtained. Fifty grams of oven dry fiber at 1.5% consistency was placed in the proportionator along with the specified amount of AKD and chemical contaminant. The pulp was mixed with agitation for 10 minutes to allow for sufficient contact. Next, Noble and Wood handsheets were made to 2.5 grams. The handsheets were put through the press only once and through the dryer two times with the felt side against the metal drum. The handsheets were conditioned in a temperature and humidity controlled room for approximately one week.

The methodology for the fiber-borne chemical contaminants can be seen in Appendix I, Diagram II. Once again, a 75/25 softwood/hardwood mix was refined in the Valley Beater in the wet lab until a 450 Canadian Standard Freeness was obtained. Fifty grams of oven dry fiber at 1.5% consistency was paced in the proportionator along with the specified amount of chemical contaminant only. The pulp was mixed with agitation for 10 minutes to allow for sufficient contact. The pulp was washed and dried by making Noble and Wood handsheets to simulate recycled pulp. The sheets were conditioned a temperature and humidity controlled room for two days. The sheets were redispersed in the British disintegrator for one minute. The pulp was then placed in the proportionator, specific amount of AKD added, and agitated for 10 minutes to allow for sufficient contact. Next, Noble and Wood handsheets were made to 2.5 grams. The handsheets were put through the press only once and through the drier two times with the felt side against the metal drum. The handsheets were conditioned in a temperature and humidity controlled room for approximately one week.

The tests conducted on the handsheets were the Hercules Size Test and the Contact Angle or Wettibility Test.

RESULTS AND DISCUSSION

CONTROL

The control level of sizing was with the virgin fiber and the 0.70 kilograms per metric ton of AKD. The first set of sheets that were made with just the control had a faster drainage time, under 30 seconds. The second set of sheets that were made were with a different Noble and Wood box. The drainage time increased dramatically, over 1.0 minute. The difference between the HST values can be seen in Appendix II, Graph II, and the difference between the contact angles can be seen in Graph III. The faster drainage time had a lower HST value and contact angle. This is due to the loss of fines. The faster the drainage, the larger loss of fines. Fines are an intricate part of retaining the sizing agent. The fines absorb the sizing agent and increase the HST values and contact angle. This is why the larger drainage time had higher HST values and higher contact angles. The larger drainage time became the control for the experiment. Therefore, the control for the HST is 749.2 seconds and the contact angle is approximately 100 degrees.

RETENTION AID

The results for the chemical contaminant of retention aid can be seen in Appendix II, Graph IV for the HST and Graph V and Graph VI for the contact angles.

The water-borne retention aid followed the expected results because the retention aid increased the sizing. But, as the level of retention aid increased the value of the HST did not increase. The values stayed almost level. The idea of reversion was first suggested. But, literature states that reversion does not occur in unfilled handsheets made with AKD. Therefore, the level HST values show that the amount of AKD retained was found at the lowest level of retention aid. Increasing the retention aid does not help the retention of the sizing by increasing levels and would only cost the papermakers more money for no results.

The fiber-borne retention aids increased the HST values by two for the lowest level, but the HST values decreased as the level of retention aid increased. This is due to a surplus of cationic retention aid adhering to the fiber before the sizing agent is introduced. Then when the cationic AKD is introduced into the pulp, there is minimal anionic surface area for the cationic sizing agent to adhere to. Therefore, low amounts of fiber-borne retention aid increase values, but surplus retention aid decrease HST values.

The results for the contact angle for the water-borne retention aid gave the higher HST values higher contact angles. The opposite is true for the fiber-borne retention aid. The higher HST values had the lower contact angles.

DEFOAMER

The results for the chemical contaminant of defoamer can be seen in Appendix II, Graph VII for the HST and Graph VIII and Graph IX for the contact angles.

The defoamer followed the expected results for the water-borne. The increase in defoamer gave decreased HST values with all values below the control HST value. The fiber-borne defoamer gave dramatically different results. The trend of increasing defoamer giving decreasing values of HST continued, but the levels of the HST values were all above the control level. Therefore, the lower amounts of fiber-borne defoamer increased sizing. If the decreasing trend follows though, the HST value will eventually go below the control level.

The results of the contact angle are the same as the retention aid. The water-borne defoamer showed the higher level of HST gave the higher contact angle, while the fiber-borne did the opposite. With the fiber-borne the lower HST values gave the higher contact angle.

BIOCIDE

The results for the chemical contaminant of biocide can be seen in Appendix II, Graph X for the HST and Graph XI and Graph XII for the contact angles.

The biocide HST values for the water-borne did stay below the control level of the size; but, as the level of biocide increased, the HST values increased. Biocide is detrimental to sizing and should decrease it. If more time was available for experimentation, then more sheets would have been made to see if increasing the biocide level would increase the HST values above the control size level. The level of the HST values could increase, stay constant, or decrease if the level of biocide increased over the 0.6 milliliters that was used.

The biocide HST values for the fiber-borne did not give the expected results. Once again, the fiber-borne chemical contaminants increased the HST values. With the biocide, the increasing of the level of biocide gave higher HST values.

The results for the contact angle are the same as the defoamer and retention aid. The water-borne biocide showed that the highest HST values gave the higher contact angle, while the fiber-borne showed that the lower HST values gave the higher contact angle.

WET STRENGTH

The results for the chemical contaminant of wet strength can be seen in Appendix II, Graph XIII for the HST and Graph XIV and Graph XV for the contact angles.

The results for the water-borne wet strength gave the expected results. As the level of wet strength increased, the HST value decreased. The decrease in sizing is due to the interference of the fiber-to-fiber bonding that is occurring with the wet strength. Therefore, the increase in the level of bonding that is occurring because of the wet strength causes a decrease in the HST values or AKD retention.

The results for the fiber-borne wet strength were unexpected. The HST values increased as the level of wet strength increased. The wet strength fiber-to-fiber bonding occurs before the sizing agent is added. Therefore, the fiber-to-fiber bonding does not effect the AKD adherence to the fiber and fines.

The results of the contact angle follow the same results as the other chemical contaminants, except for a slight variation with the water-borne. The water-borne wet strength showed different results than the other contaminants. The highest level of HST gave the lower contact angle, which is a direct opposite of the rest of the contaminants. The fiber-borne wet strength did follow the trend set by the rest of the contaminants. The lowest HST value gave the highest contact angle.

CONCLUSION

1) RETENTION AID
   - a) Water-borne retention aids increase the sizing response.
   - b) Fiber-borne retention aids increase the sizing response, but the response decreases as more contaminants is added.

2) DEFOAMER
   - a) Water-borne defoamer lowers the level of sizing response.
   - b) Fiber-borne defoamer increases the level of sizing response.

3) BIOCIDE
   - a) Water-borne biocide lowers the level of sizing response.
   - b) Fiber-borne biocide increases the level of sizing response.

4) WET STRENGTH
   - a) Water-borne wet strength decreases the sizing response as more wet strength contaminant is added.
   - b) Fiber-borne wet strength increases the sizing response.

5) CONTACT ANGLE
   - a) Water-borne chemical contaminants give high contact angles for high HST values.
   - b) Fiber-borne chemical contaminants give high contact angles for low HST values.

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APPENDIX I

Methodology
Water-borne
Daigram I

75/25 SW/HW

Refined to 450 csf

AKD sizing

Chemical Contaminant

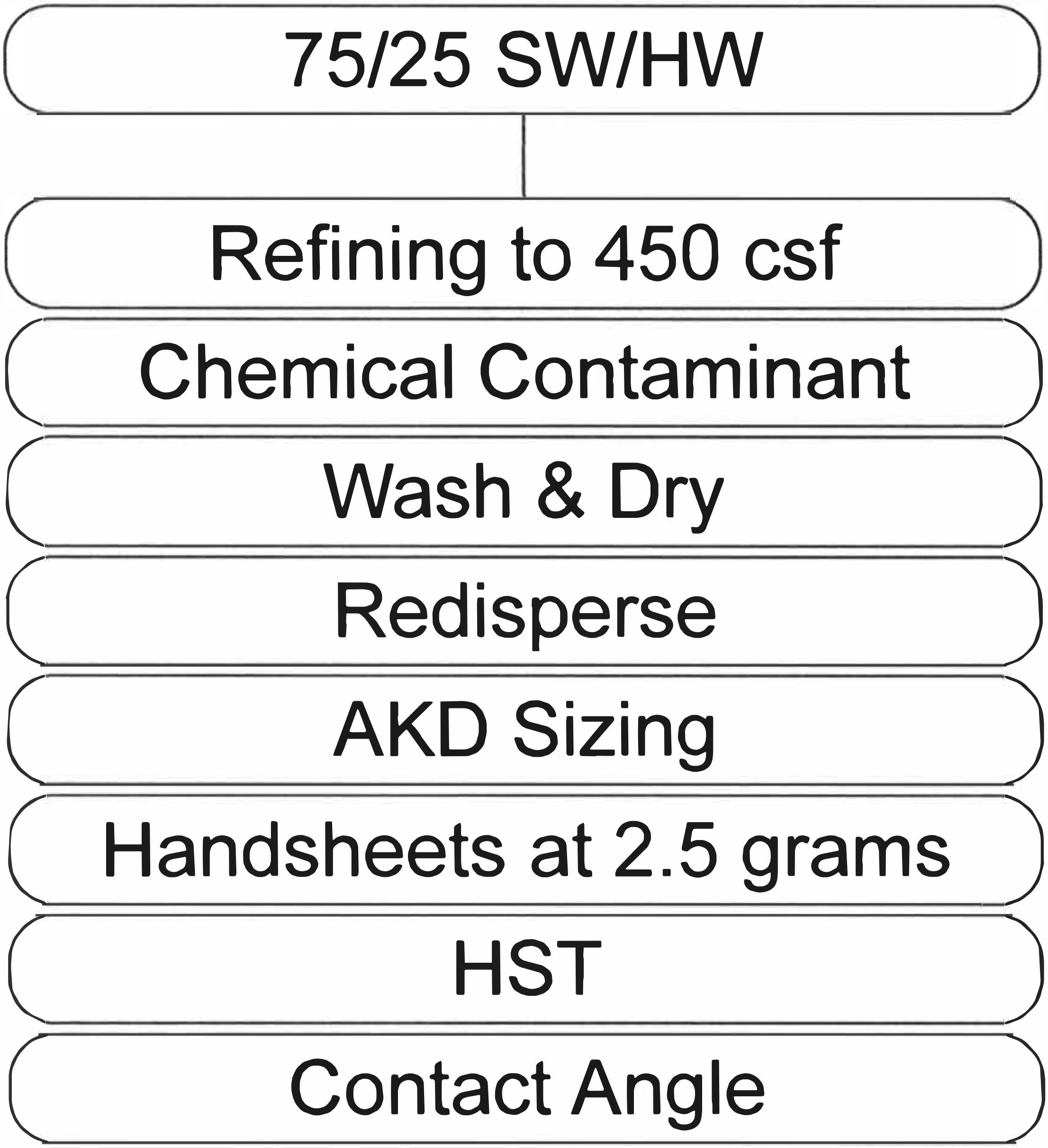
Handsheets to 2.5 grams

HST

Contact Angle

Methodology
Fiber-borne

Diagram II



75/25 SW/HW

Refining to 450 csf

Chemical Contaminant

Wash & Dry

Redisperse

AKD Sizing

Handsheets at 2.5 grams

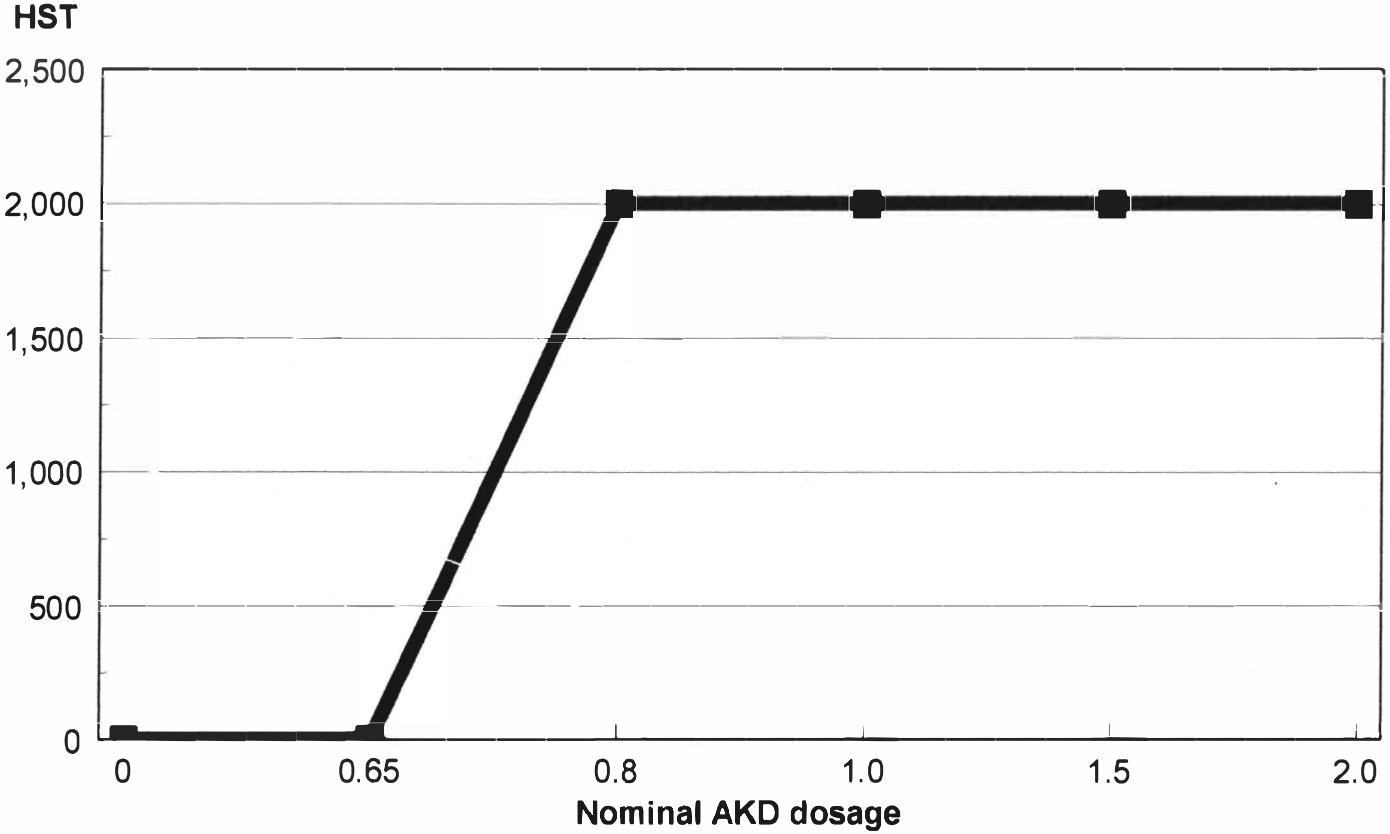
HST

Contact Angle

APPENDIX II

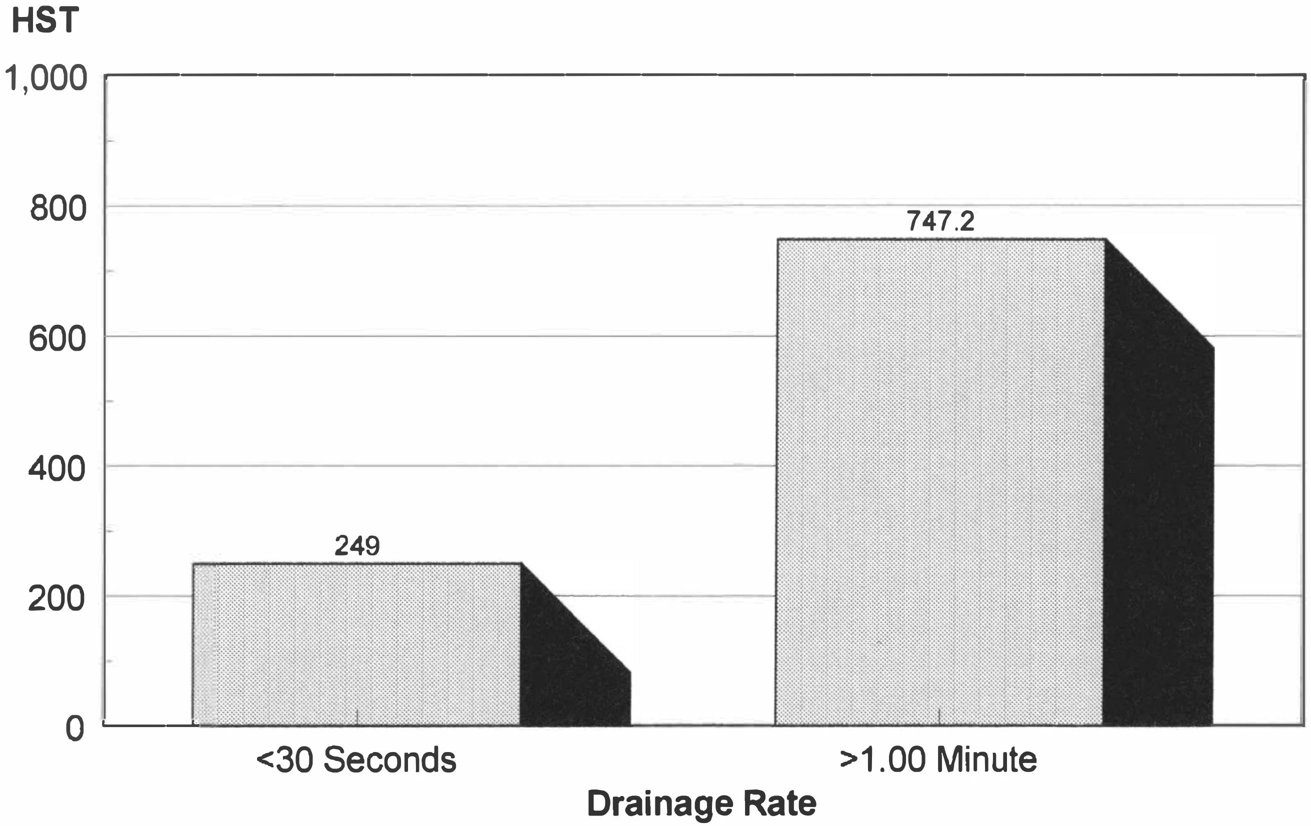
HST vs. nominal AKD dosage

Graph I

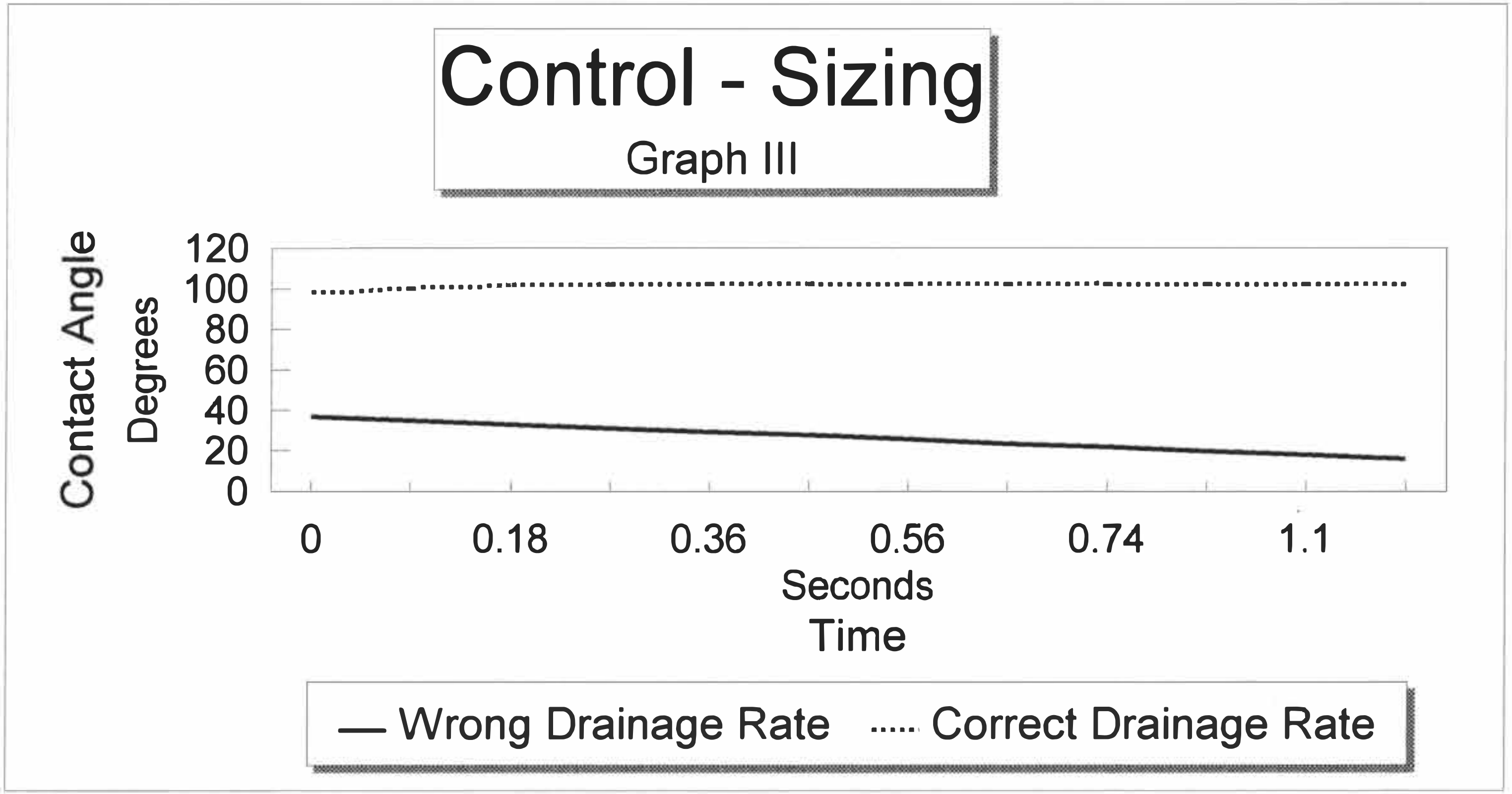


Control
Sizing Agent

Graph II

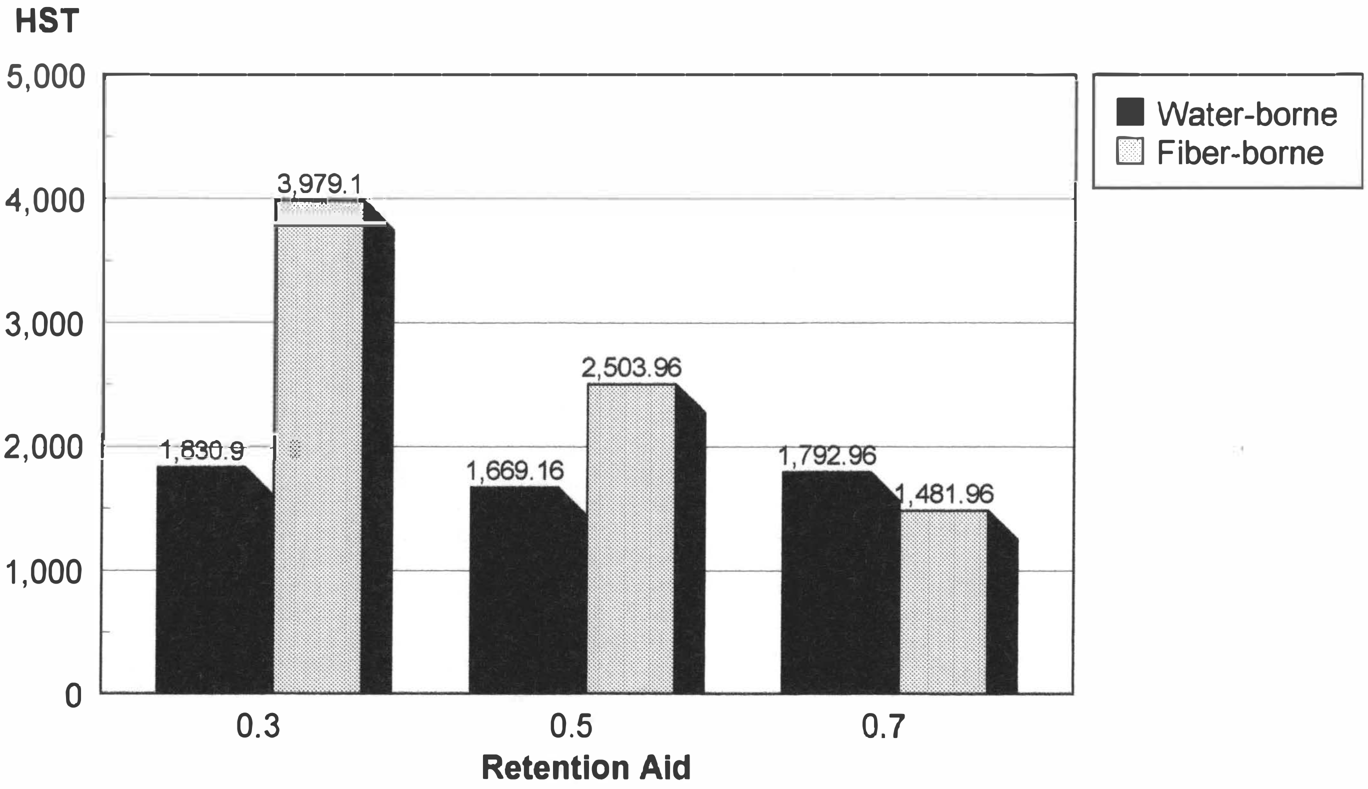


Standard Deviation for < 30 Seconds : 70
Standard Deviation for 1.00 Minute : 76


Control - Sizing
Graph III
Contact Angle
Degrees
120
100
80
60
40
20
0
0
0.18
0.36
0.56
0.74
1.1
Seconds
Time
Wrong Drainage Rate
Correct Drainage Rate

Retention Aid

Graph IV

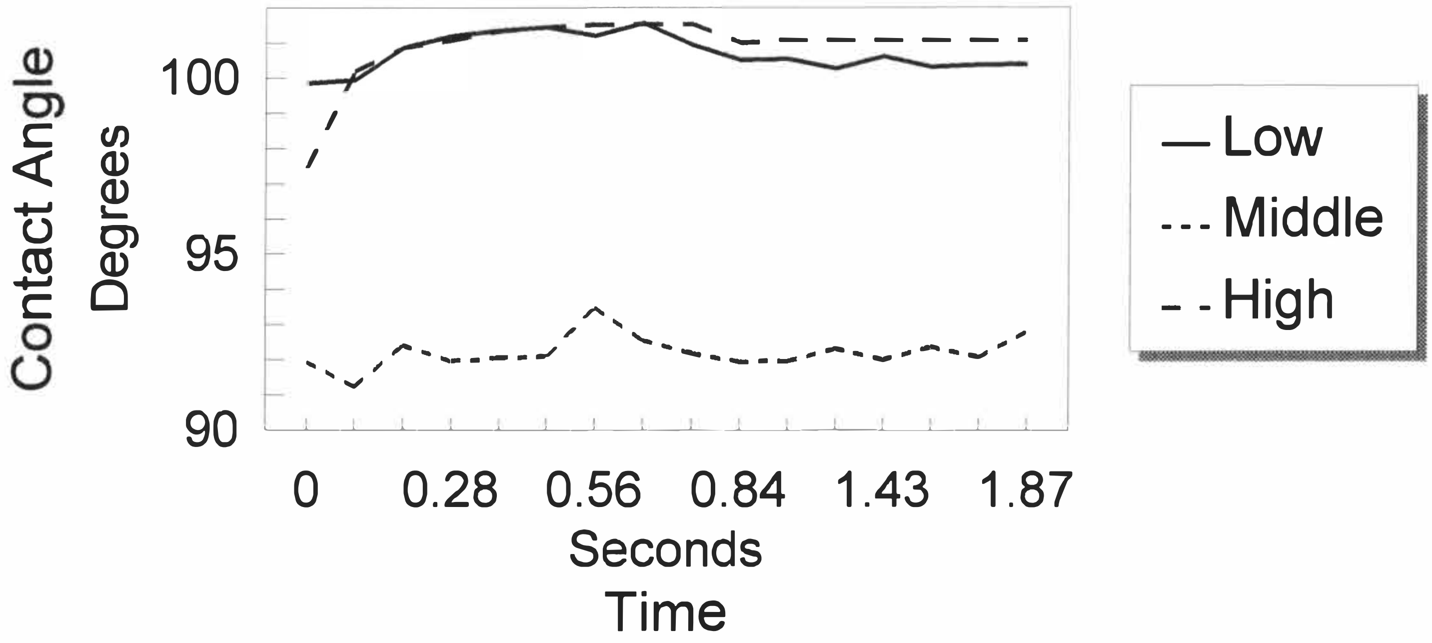


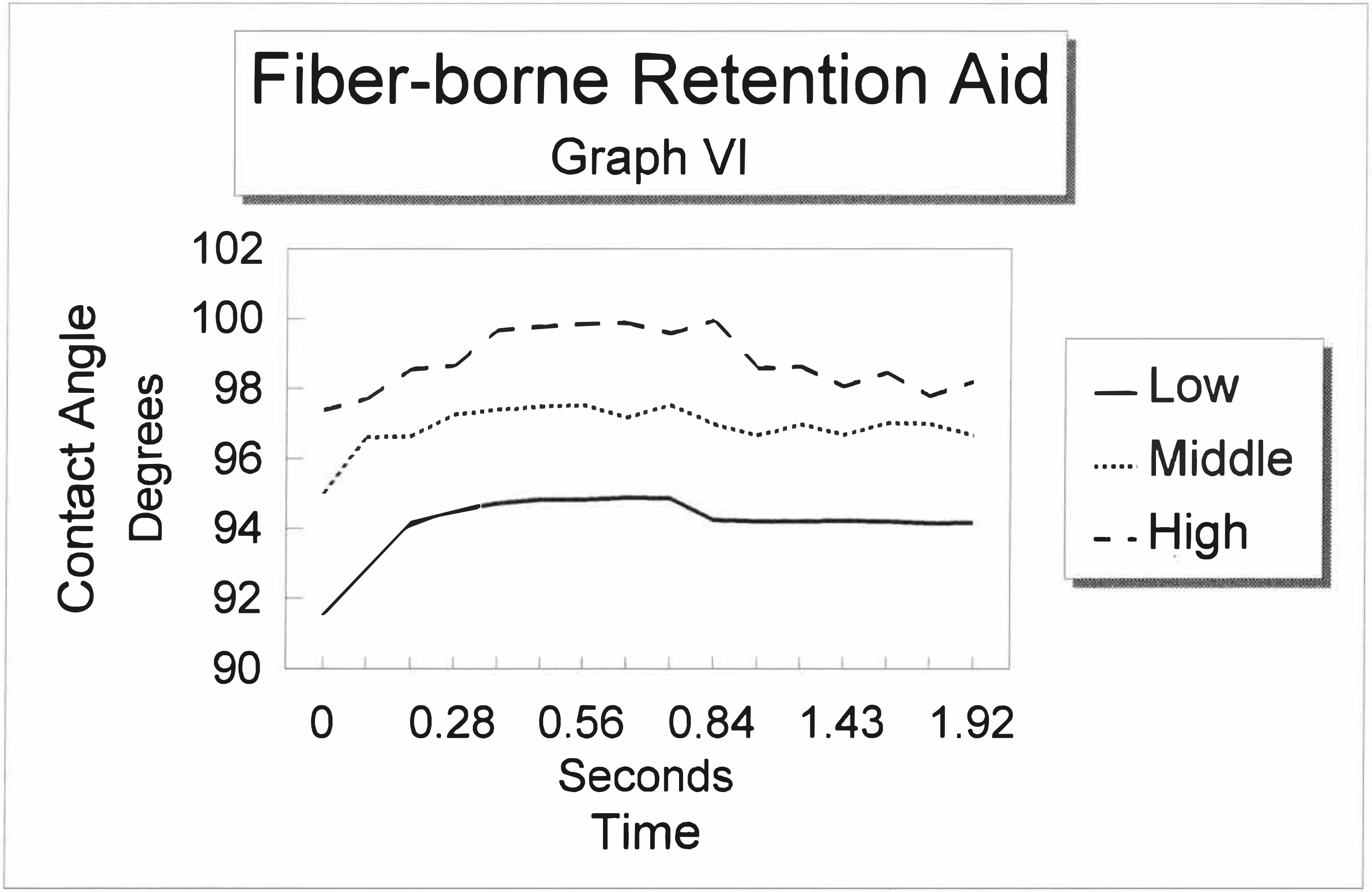
Standard Deviation for Control : 42, 97, 49

Standard Deviation for Recycle : 176, 198, 165

Water-borne Retention Aid

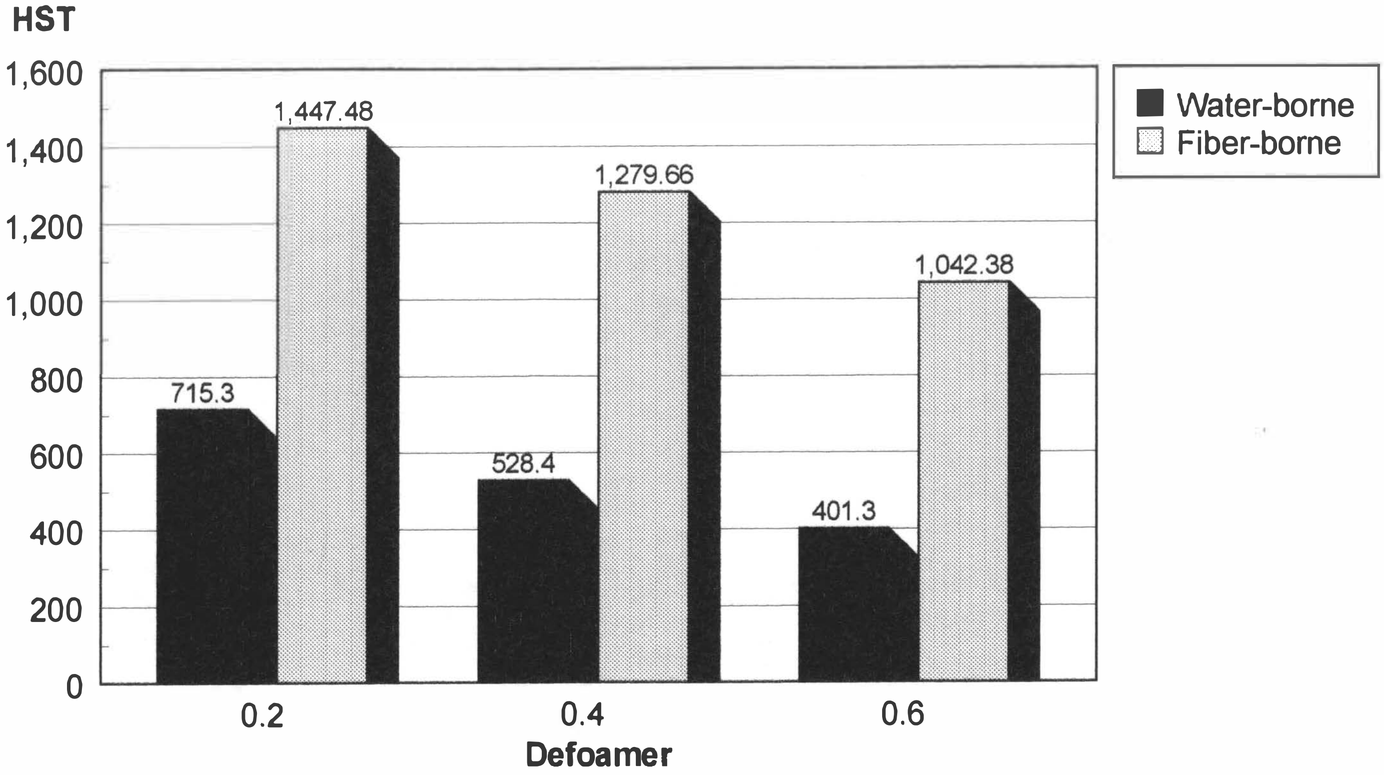
Graph V




Fiber-borne Retention Aid
Graph VI
Contact Angle
Degrees
102
100
98
96
94
92
90
0
0.28
0.56
0.84
1.43
1.92
Seconds
Time
Low
Middle
High

Defoamer

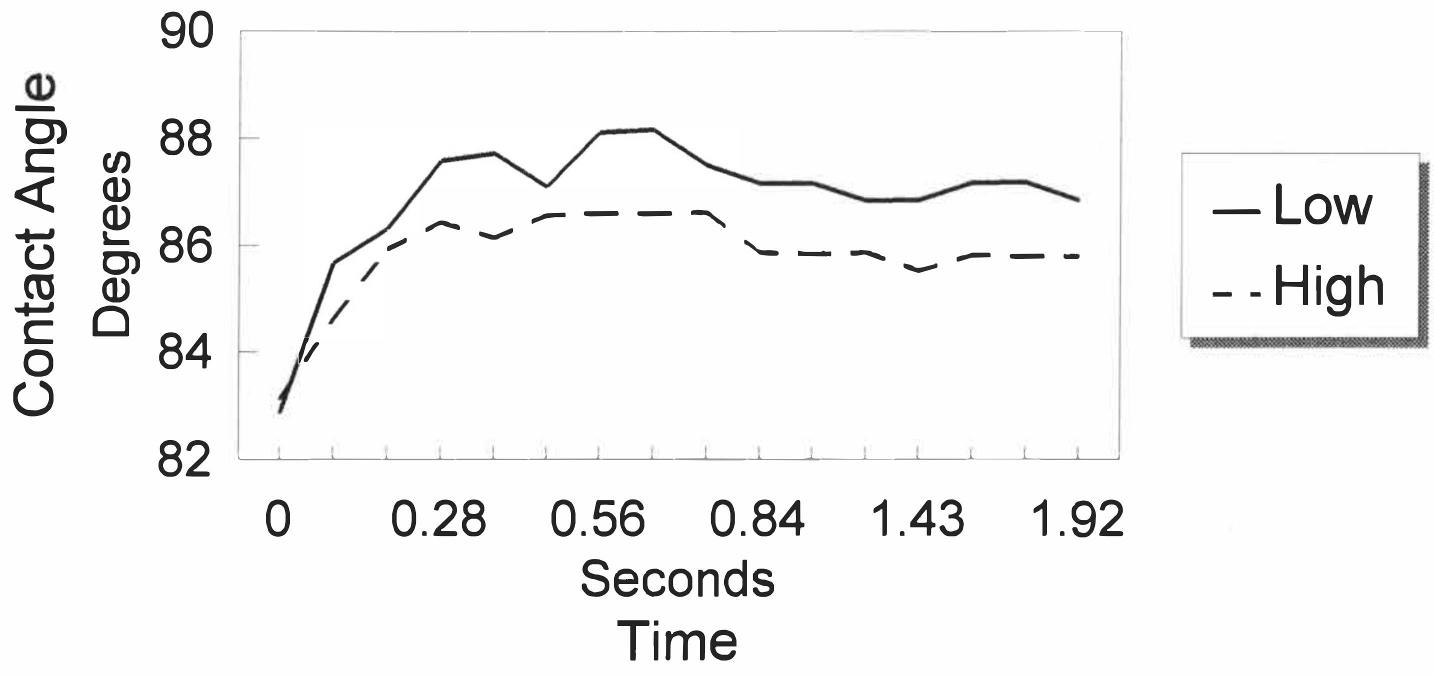
Graph VII



Standard Deviation for Control : 85, 97, 102
Standard Deviation for Recycle : 82, 79, 66

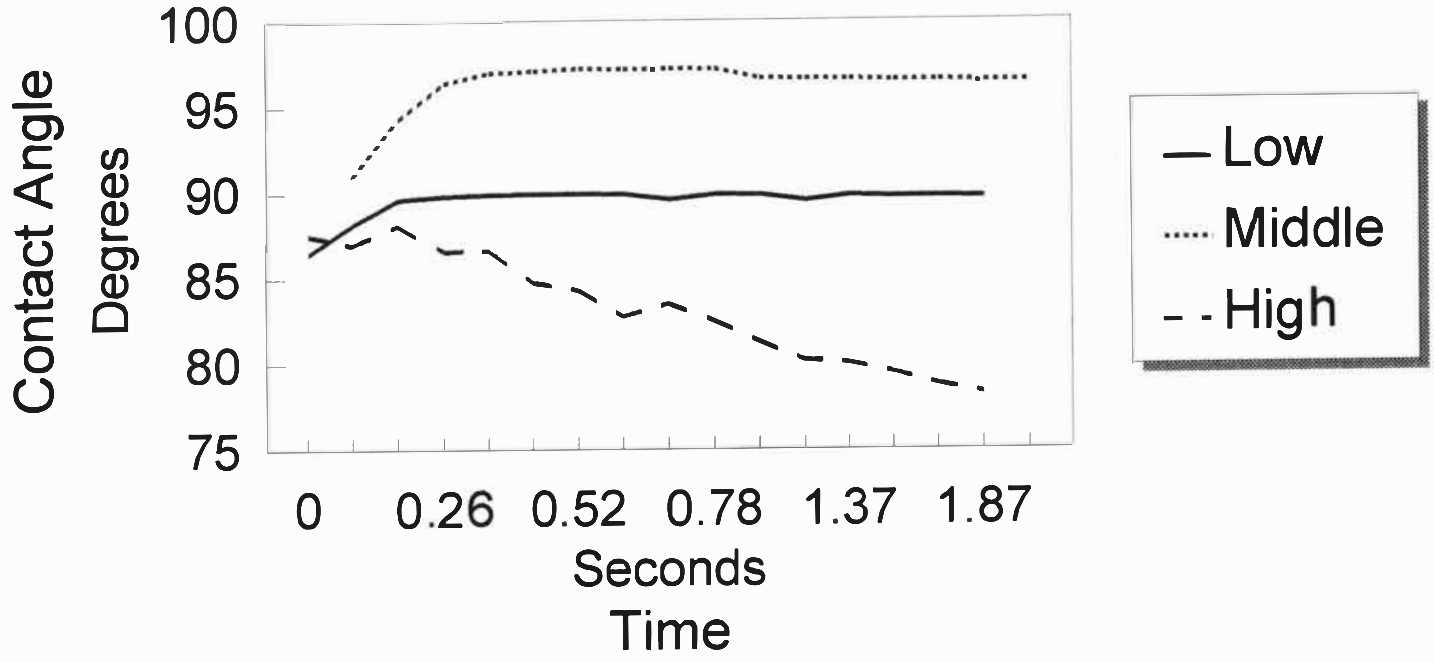
Water-borne Defoamer

Graph VIII



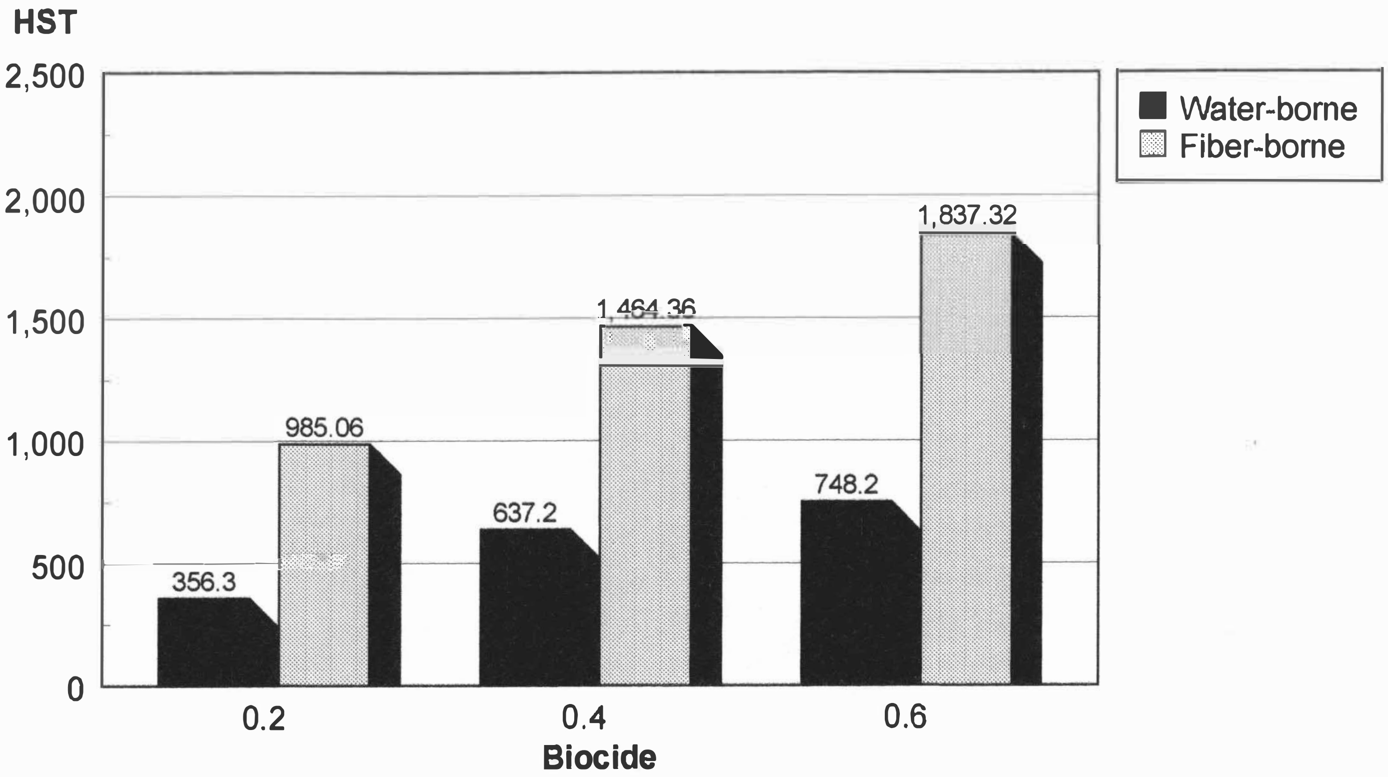
Fiber-Borne Defoamer

Graph IX

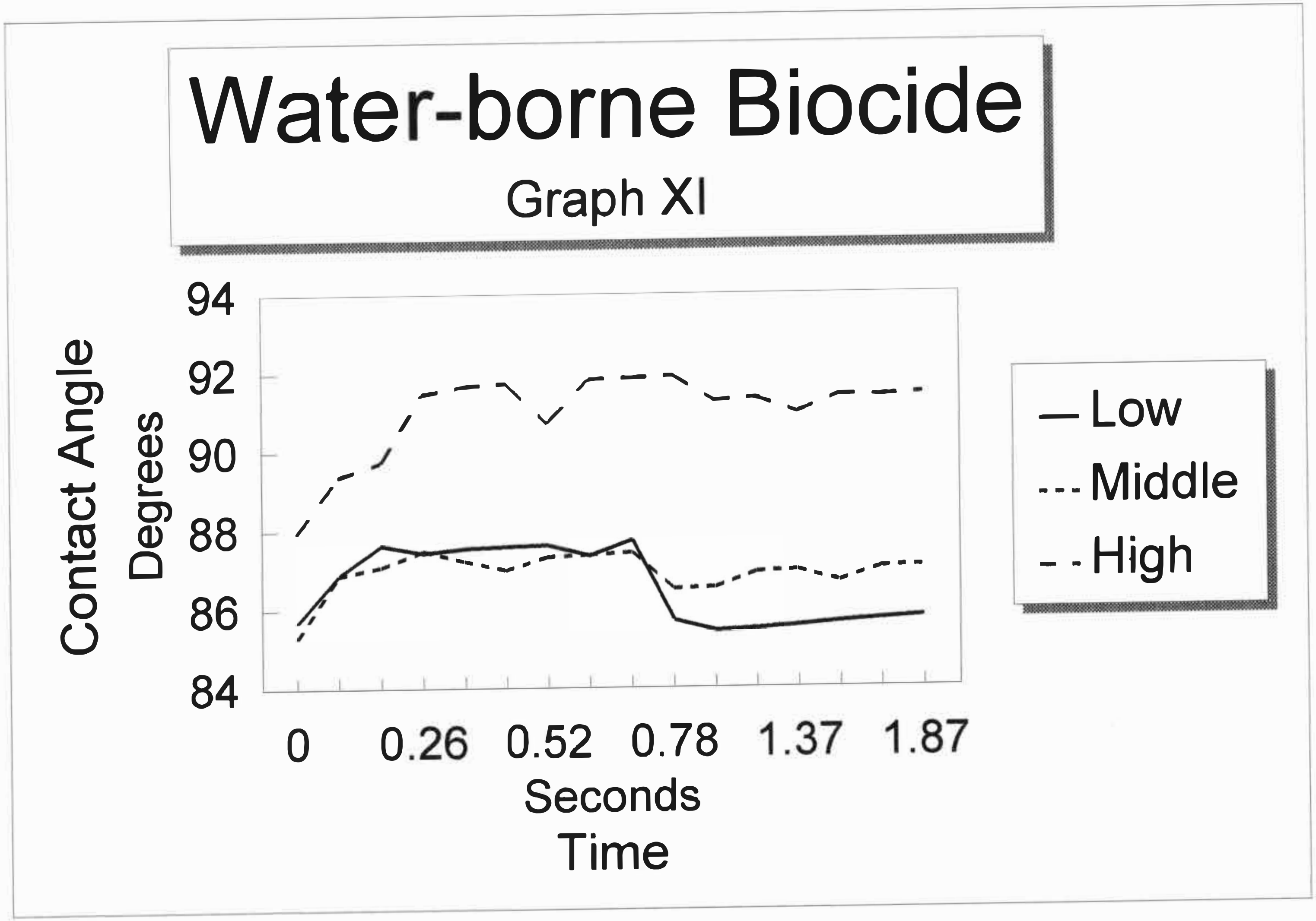


Biocide

Graph X

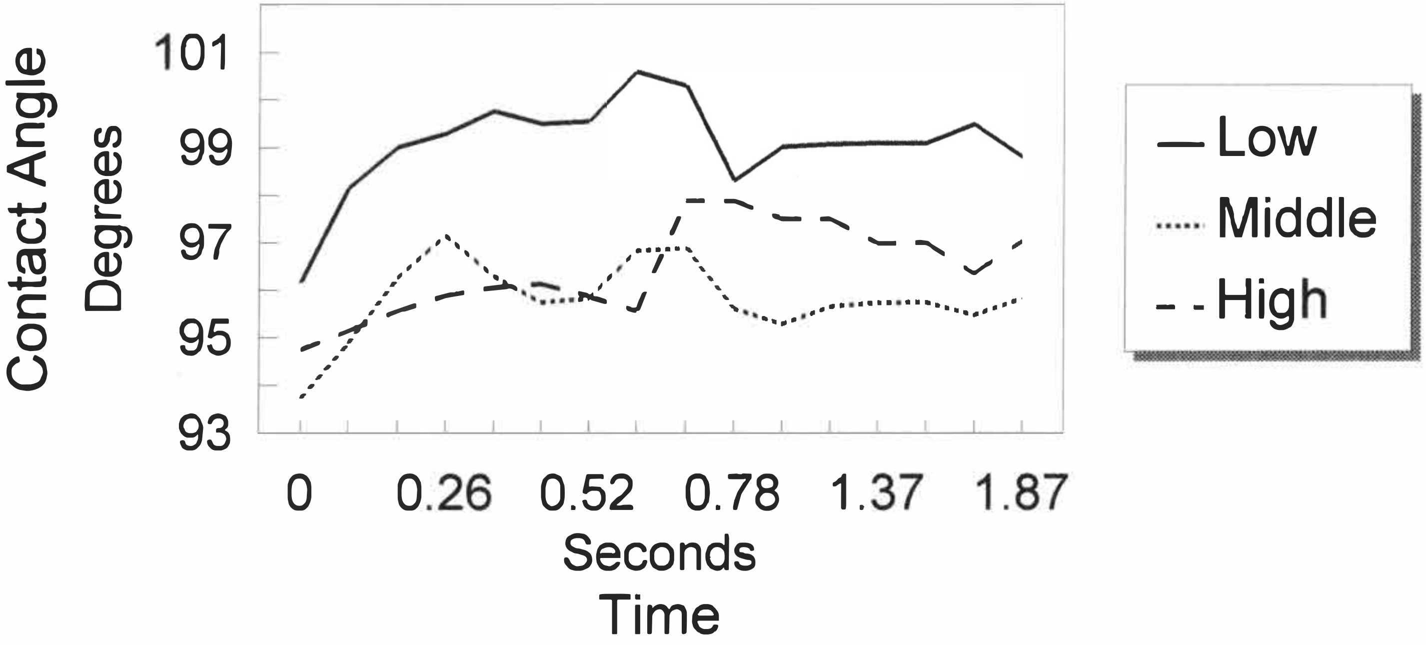


Standard Deviations for Control : 112, 104, 62
Standard Deviations for Recycle : 101, 68, 106


Water-borne Biocide
Graph XI
Contact Angle
Degrees
94
92
90
88
86
84
0
0.26
0.52
0.78
1.37
1.87
Seconds
Time
Low
Middle
High

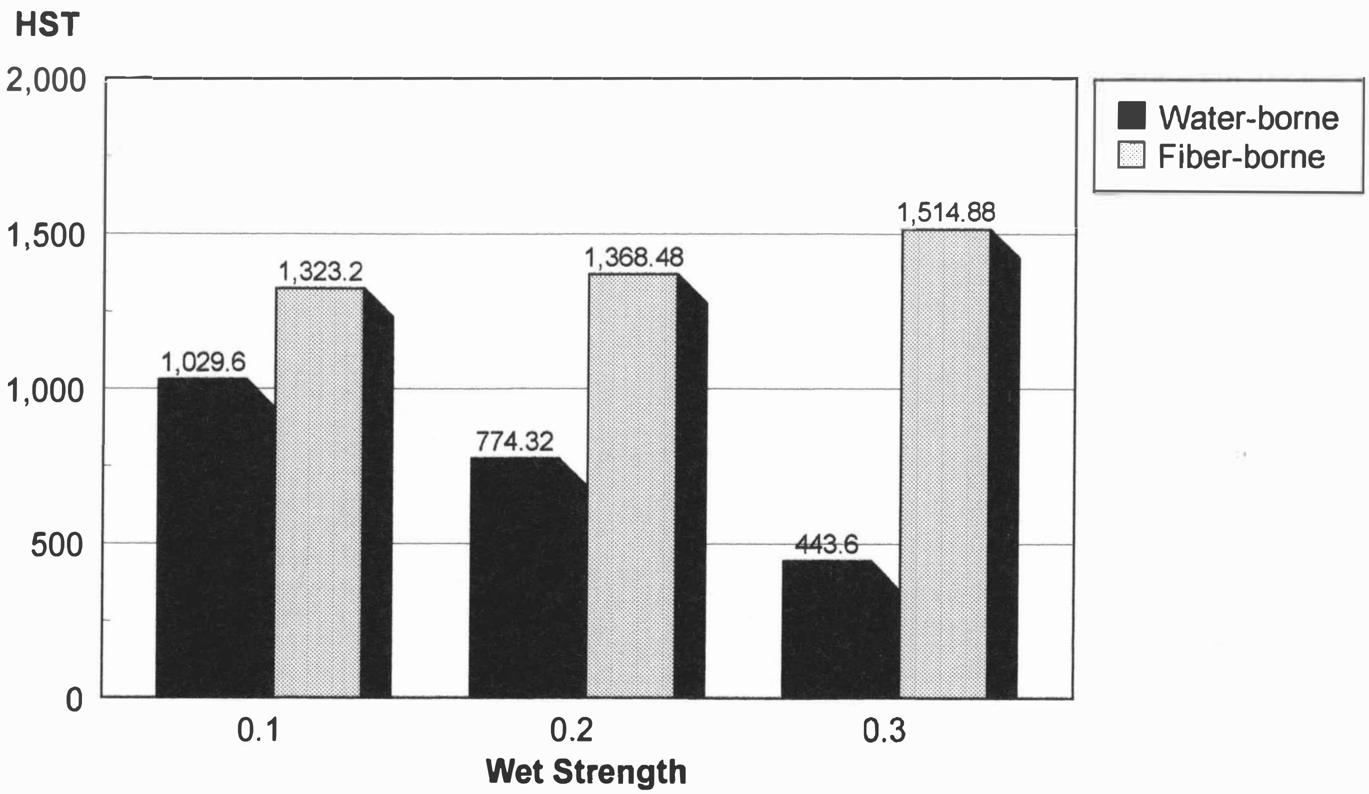
Fiber-borne Biocide

Graph XII



Wet strength

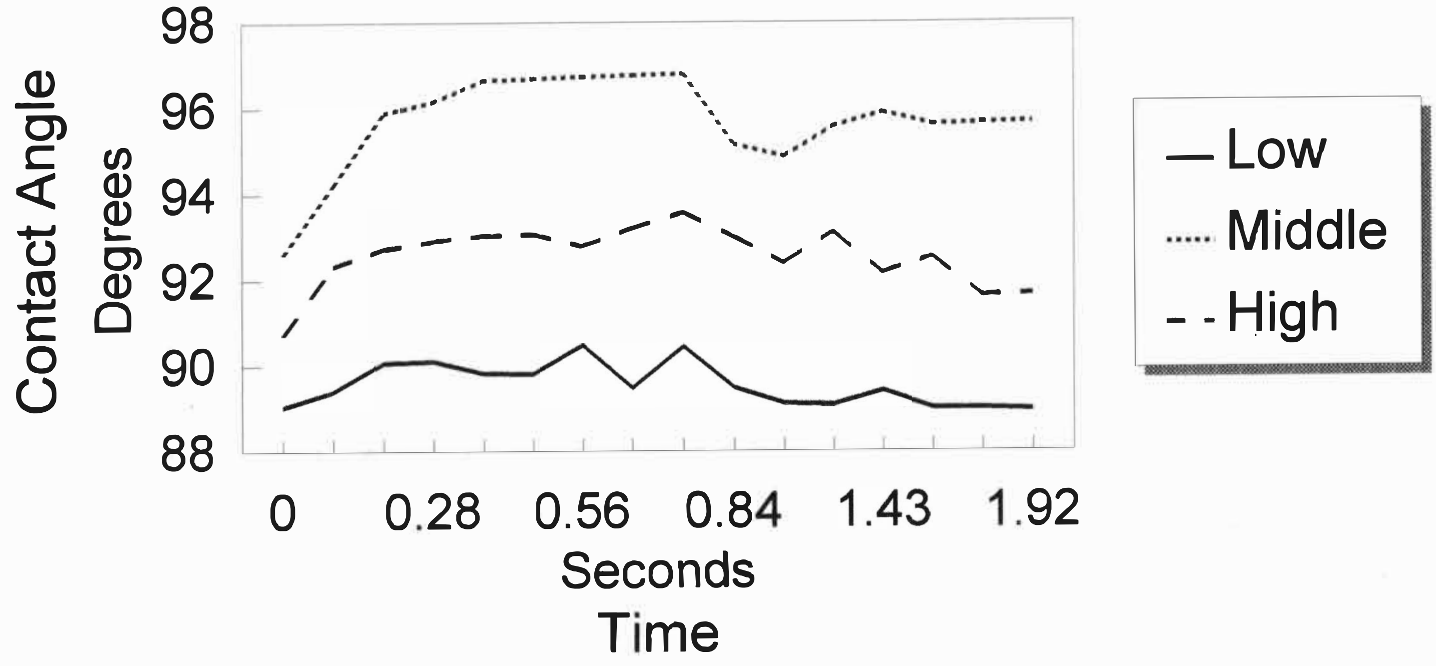
Graph XIII

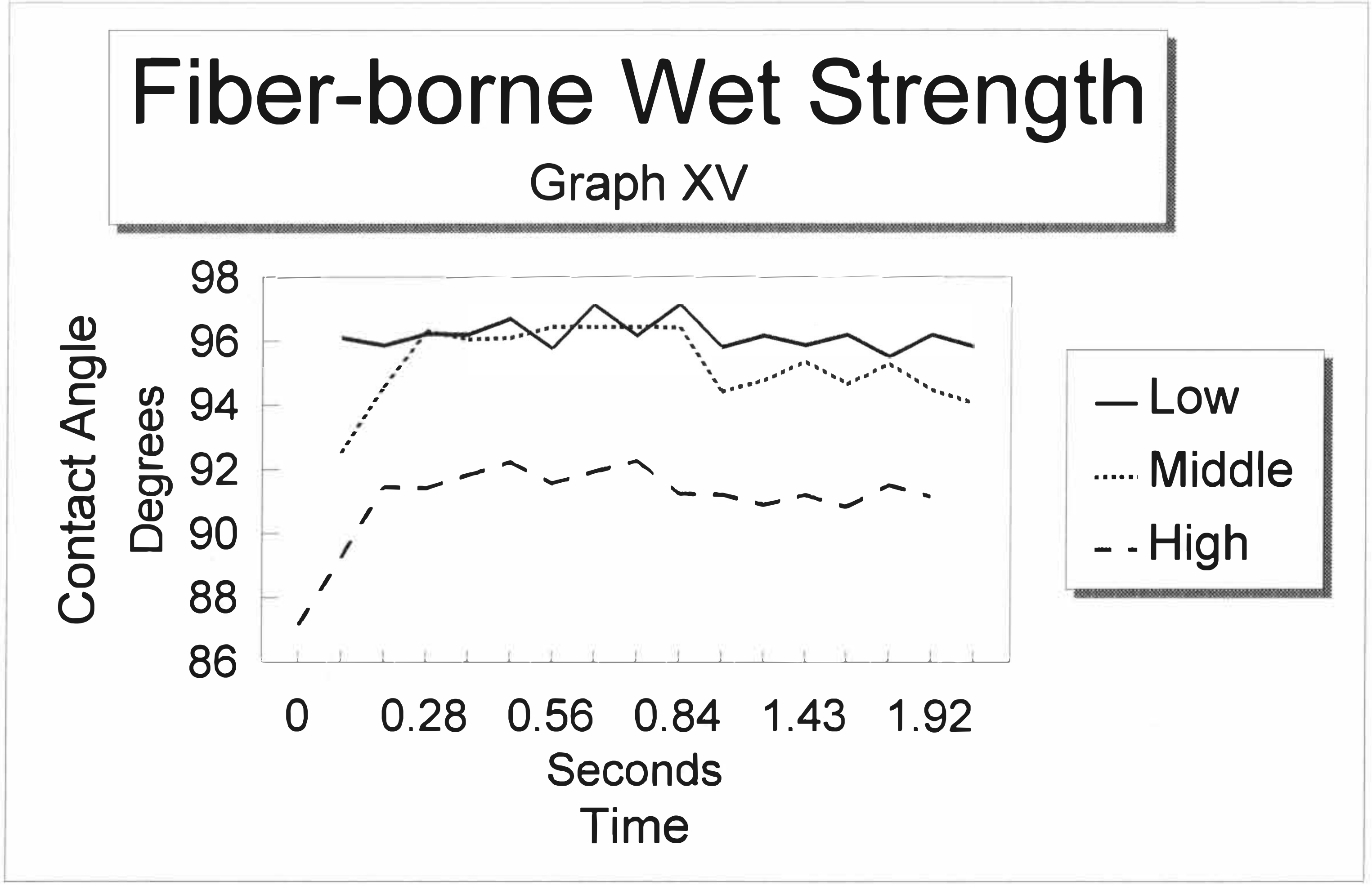


Standard Deviations for Control : 69., 101, 67
Standard Deviations for Recycle : 53, 110, 75

Water-borne Wet Strength

Graph XIV




Fiber-borne Wet Strength
Graph XV
Contact Angle
Degrees
98
96
94
92
90
88
86
0
0.28
0.56
0.84
1.43
1.92
Seconds
Time
Low
Middle
High

APPENDIX III

Water-borne Chemical Contaminants
Table 1

Contaminants	Level of Addition	HST	Standard Deviation
Control	0	749.2	76
Retention Aid	0.3	1830.9	42
	0.5	1669.16	97
	0.7	1792.96	49
Defoamer	0.2	715.3	85
	0.4	528.4	97
	0.6	401.3	102
Biocide	0.2	356.3	112
	0.4	637.2	104
	0.6	748.2	62
Wet Strength	0.1	1029.6	69
	0.2	774.32	101
	0.3	443.6	67

Fiber-borne Chemical Contaminants
Table 2

Contaminants	Level of Addition	HST	Standard Deviation
Control	0	749.2	76
Retention Aid	0.3	3979.1	176
	0.5	2503.96	198
	0.7	1481.96	165
Defoamer	0.2	1447.48	82
	0.4	1279.66	79
	0.6	1042.38	66
Biocide	0.2	985.06	101
	0.4	1464.36	68
	0.6	1837.32	106
Wet Strength	0.1	1323.2	53
	0.2	1368.48	110
	0.3	1514.88	75